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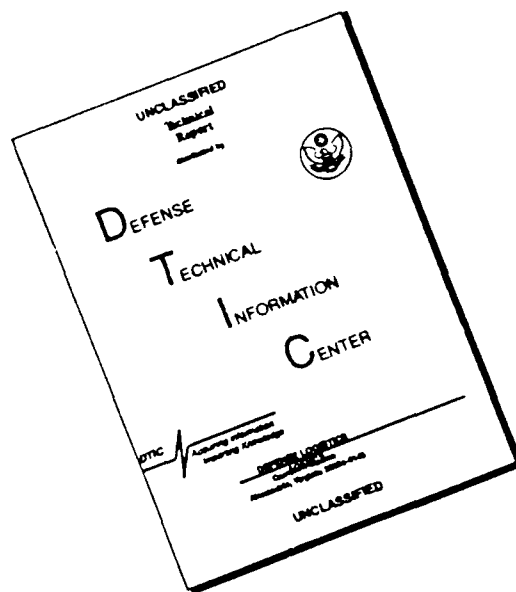
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FINAL REPORT

"Molecular Jet Studies of vdW Clusters and Solvation"

by

E.R. Bernstein

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Department of Chemistry
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Fort Collins, Colorado 80523

October 1991

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The work completed during this period has been carried out by many co-workers supported by the ONR and has been reported in published papers and more than 50 Technical Reports.

The people involved have been both graduate students and post doctoral fellows.

Breen, P. J.	(PD)	Menapace, J. A.	(GS)
Disselkamp, R.	(PD)	Moreno, P.	(PD)
Grassian, V. H.	(PD)	Nimlos, M. R.	(PD)
Hineman, M.	(PD)	Nowak, R.	(PD)
Hsu, S.	(PD)	Shang, Q. Y.	(PD)
Im, H. S.	(GS)	Warren, J. A.	(PD)
Kim, S. K.	(PD)	Young, M. A.	(PD)
Li, S.	(PD)		

Together in one report below are the abstracts of the published and to be published papers from this work. They include studies of the structure of nonrigid molecules, the formation of clusters and dimers, liquid cluster structure, chemical reaction studies, and studies of cluster dynamics.

1988 to present: see attached

Papers in press but not published: see attached

Benzene clustered with N₂, CO₂, and CO: Energy levels, vibrational structure, and nucleation

R. Nowak, J. A. Menapace,^{a)} and E. R. Bernstein

Condensed Matter Sciences Laboratory, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

(Received 3 February 1988; accepted 21 April 1988)

Two-color time-of-flight mass spectroscopy is employed to study the van der Waals (vdW) clusters of benzene(N₂)_n ($n \leq 8$), benzene(CO₂)_n ($n \leq 7$), and benzene(CO)_n ($n = 1, 2$) created in a supersonic molecular jet. Potential energy calculations of cluster geometries, normal coordinate analysis of vdW vibrational modes, and calculations of the internal rotational transitions are employed for the assignment of the benzene(solvent)₁ cluster spectra in the 0₀⁰ and 6₀¹ regions of the benzene ¹B_{2u} ← ¹A_{1g} transition. The respective vibronic and rotational selection rules for these clusters are determined based on the appropriate point groups and molecular symmetry groups of the clusters. Good agreement between the calculated and experimental spectra is obtained with regard to the vdW vibrational and internal rotational modes. The solvent molecules rotate nearly freely with respect to benzene about the benzene-solvent bond axis in the benzene(solvent)₁ clusters. In the excited state a small ~20 cm⁻¹ barrier to rotation is encountered. Studies of larger clusters ($n > 2$) reveal a broad red shifted single origin in the 6₀¹ spectra. A linearly increasing cluster energy shift is observed as a function of cluster size. The cluster energy shifts are not saturated by one solvent molecule on each side of the aromatic ring; several solvent molecules effectively interact with the solute π electronic cloud. Both homogeneous and inhomogeneous nucleation take place for the clusters studied depending on the ratio of the solvent-solvent binding energy to the cluster binding energy.

Spectroscopic Observation and Geometry Assignment of the Minimum Energy Conformations of Methoxy-Substituted Benzenes

P. J. Breen,^{1a,b} E. R. Bernstein,^{*1a} Henry V. Secor,^{1c} and Jeffrey I. Seeman^{*1c}

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, and the Philip Morris Research Center, P.O. Box 26583, Richmond, Virginia 23261. Received April 14, 1988

Abstract: Optical spectroscopic data are presented for methoxybenzene, the three methoxytoluenes, 1-ethyl-4-methoxybenzene, and 1,2- and 1,3-dimethoxybenzene cooled and isolated in a supersonic jet expansion. Each unique stable conformation of the sterically unencumbered methoxybenzenes displays a unique and assignable spectrum; the interpretation of these spectra leads to the assignment of specific molecular geometries for each system. The minimum energy conformation of the methoxy group with respect to the ring is shown to be a planar conformation in which the methoxy group lies in the plane of the ring. The potential barrier for rotation of the ring methyl group in the methoxytoluenes is characterized from observed transitions between methyl group rotational levels which accompany the electronic transition. The meta isomer exhibits a large barrier to methyl rotation in S₁ ($V_3 \sim 520$ cm⁻¹) whereas the methyl group in the ortho and para isomers is nearly freely rotating ($V_3 \leq 50$ cm⁻¹). The dimethoxybenzenes exhibit spectral features due to torsions of the methoxy groups. Substantial barriers to methoxy group rotation ($V_1 = 500$ cm⁻¹, $V_2 = 100$ cm⁻¹ for ortho, V_1 and $V_2 \sim 2000$ –5000 cm⁻¹ for meta) are established; again the torsional barrier appears to be highest for the meta or 3-position on the ring. The presence of cross kinetic and potential terms between methoxy groups is further suggested for the ortho isomer.

A Study of Nonrigid Aromatic Molecules. Observation and Spectroscopic Analysis of the Stable Conformations of Various Alkylbenzenes by Supersonic Molecular Jet Laser Spectroscopy[†]

Jeffrey I. Seeman,^{*,1a} Henry V. Secor,^{1a} P. J. Breen,^{1b,c} V. H. Grassian,^{1b} and E. R. Bernstein^{*,1b}

Contribution from the Philip Morris Research Center, P.O. Box 26583, Richmond, Virginia 23261, and the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. Received April 26, 1988

Abstract: The technique of supersonic molecular jet laser spectroscopy was used to determine the stable conformations of a series of alkylbenzenes. This study demonstrates, for the first time, the sensitivity of molecular jet spectroscopy in determining both the number of stable conformations as well as the geometry of various ethyl, propyl, and butyl substituents relative to the aromatic ring. Different rotamers with low barriers to interconversion, <5 kcal/mol, can be isolated in the supersonic jet expansion. Each observed conformation exhibits its own spectroscopic origin ($S_1 \leftarrow S_0$ transition) in a two-color time-of-flight mass spectrum (TOFMS). The number of stable conformations is then used to determine the minimum energy geometries of the substituent group. Previous identification of individual molecular conformations for such low barriers to interconversion has not been attainable with conventional techniques such as variable-temperature NMR.

Spectroscopy, Structure, and Proton Dynamics of 2-Hydroxypyridine and Its Clusters with Water and Ammonia

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Department of Chemistry, Condensed Matter Science Laboratory, Colorado State University, Fort Collins, Colorado 80523 (Received: June 3, 1988)

The two tautomeric forms of 2-hydroxypyridine (2-HP) have been studied in a supersonic jet expansion. Time-of-flight mass spectroscopy (TOFMS) and emission spectroscopy of the lactim and lactam tautomers have been studied and are reported here. The lactim spectrum is similar to an earlier TOFMS spectrum and has its origin at $36\,136\text{ cm}^{-1}$. Evidence of mixing of the $n\pi^*$ and $\pi\pi^*$ electronic states is seen in the lactim spectrum. The mixing is removed in the disolvate water cluster but not in monosolvate clusters of ammonia or water. The lactam is shown to be nonplanar giving rise to two origins in the excitation spectrum at $29\,832$ and $29\,935\text{ cm}^{-1}$. The ammonia and water lactim cluster spectra show significant shifts to the red while the cluster spectra of the lactam show large shifts to the blue. Experimental evidence for strong hydrogen bonding in these clusters is discussed. Intramolecular and intermolecular proton transfer in 2-HP and its clusters is discussed in the context of these data.

Conformational Study of Jet-Cooled Styrene Derivatives. Demonstration of the Planarity of Nonsterically Hindered Styrenes

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Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Henry V. Secor, and Jeffrey I. Seeman^{*}

Philip Morris U.S.A. Research Center, P.O. Box 26583, Richmond, Virginia 23261 (Received: August 3, 1988; In Final Form: October 21, 1988)

One-color time-of-flight mass spectroscopy (mass-resolved excitation spectroscopy) is used to determine ground- and excited-state geometries and molecular parameters for styrene and a number of its derivatives cooled in a supersonic jet expansion. In this paper we present results for styrene and a series of sterically unhindered substituted derivatives: *trans*- β -methylstyrene, 3-methylstyrene, 4-ethylstyrene, and 4-methoxy-*trans*- β -methylstyrene (anethole). Styrene, *trans*- β -methylstyrene, and 4-ethylstyrene all exhibit one spectroscopic origin corresponding to a single conformation, whereas 3-methylstyrene and anethole exhibit two origins corresponding to syn and anti ground-state conformations. The vinyl group is concluded to be planar with respect to the aromatic ring for all of these molecules in both S_0 and S_1 . A one-dimensional methyl rotor analysis for the two conformers of 3-methylstyrene in the first excited singlet state S_1 yields the parameters for methyl rotation in the anti conformer, $B = 5.20\text{ cm}^{-1}$, $V_3 = 80.0\text{ cm}^{-1}$, and $V_6 = -15.0\text{ cm}^{-1}$ and in the more hindered syn conformer, $B = 5.95\text{ cm}^{-1}$, $V_3 = 185.0\text{ cm}^{-1}$, and $V_6 = -27.5\text{ cm}^{-1}$.

Conformational changes upon $S_1 \leftarrow S_0$ excitation in 4-dimethylaminobenzonitrile and some of its chemical analogs

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(Received 31 October 1988; accepted 16 December 1988)

One-color time-of-flight mass spectra (mass resolved excitation spectra) for jet-cooled 4-dimethylaminobenzonitrile (4-DMABN) and some of its chemical analogs, dimethylaniline (DMA), 3-dimethylaminobenzonitrile (3-DMABN), *N,N*-dimethyl-4-(trifluoromethyl)aniline (4-CF₃-DMA), and 4-(*d*₆-dimethylamino)benzonitrile (4-*d*₆-DMABN), are presented and analyzed. Near the origin of the $S_1 \leftarrow S_0$ transition the low frequency modes can be assigned to motions of the dimethylamino group for this series of molecules. The inversion motion of the dimethylamino group and the dimethylamino group torsion about the C_{ipso}-N bond (the twist coordinate) in S_1 give rise to the most prominent peaks in this spectrum. The potential parameters for the twist coordinate of 4-DMABN and DMA are quite similar in S_1 : $B = 0.546$, $V_2 = 175$, and $V_4 = 525$ cm⁻¹ for 4-DMABN and $B = 0.546$, $V_2 = 175$, and $V_4 = 515$ cm⁻¹ for DMA. The V_2 and V_4 terms are slightly larger for 3-DMABN and 4-CF₃-DMA. The inversion motion is also similar for these molecules but is more anharmonic for the para-substituted dimethylanilines, 4-DMABN and 4-CF₃-DMA, than for the meta and unsubstituted molecules. A Franck-Condon intensity analysis for the dimethylamino twist in these molecules suggests that this group in 4-DMABN is displaced in the excited state by $\sim 30^\circ$ with respect to its planar orientation in the ground state. In both solutions and monosolvate clusters of 4-DMABN with polar aprotic solvents, a low lying charge transfer (CT) state is identified in addition to the usual $\pi\pi^*$ excited state of the bare molecule. The relation between the bare molecule 4-DMABN twisting displacement upon excitation and the low lying CT state is discussed.

Determination of the Minimum-Energy Conformation of Allylbenzene and Its Clusters with Methane, Ethane, Water, and Ammonia

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(Received: November 30, 1988; In Final Form: April 20, 1989)

Supersonic molecular jet laser time-of-flight mass spectroscopy (TOFMS) is employed to determine the minimum-energy conformation of the allyl group with respect to the benzene ring of allylbenzene, 1-allyl-2-methylbenzene, and 1-allyl-3-methylbenzene. The spectra are assigned and conformations are suggested with the aid of molecular orbital-molecular mechanics (MOMM-85) calculations. Based on the experimental and theoretical results, the minimum-energy conformer is found to have $\tau_1(\text{C}_{\text{ortho}}-\text{C}_{\text{ipso}}-\text{C}_\alpha-\text{C}_\beta) = \text{ca. } 90^\circ$ (i.e., the allyl group is essentially perpendicular to the plane of the benzene ring) and $\tau_2(\text{C}_{\text{ipso}}-\text{C}_\alpha-\text{C}_\beta-\text{C}_\gamma) = \pm 120^\circ$ (i.e., the olefin $\text{C}=\text{C}$ bond is eclipsed with the $\text{C}_\alpha-\text{H}_\alpha$ bond). The TOFMS of allylbenzene clustered with methane, ethane, water, and ammonia are also presented. A Lennard-Jones potential energy 6-12-1 atom-atom calculation is used to characterize the structures of these clusters. Experiments and calculations demonstrate that the four different solvent molecules studied can form stable clusters with allylbenzene by coordinating to the π -system of the allyl substituent in addition to that of the aromatic ring.

Supersonic Jet Studies of Fluorene Clustered with Water, Ammonia, and Piperidine

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Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523 (Received: May 30, 1989)

Mass-resolved excitation spectroscopy and dispersed emission spectroscopy are employed to study van der Waals (vdW) clusters of jet-cooled fluorene with ammonia, water, and piperidine. For fluorene(H_2O)₁ and fluorene(NH_3)₁ clusters, cluster geometries and binding energies can be suggested based on the experimental results and Lennard-Jones (LJ) potential (6-12-1) energy calculations. As the number of solvent molecules in the cluster is increased, spectra of the clusters become more complex and broad probably due to the many possible stable configurations for these vdW clusters. Although the $\text{p}K_a$ for fluorene in its first excited singlet state (Förster cycle calculations) is quite acidic (-8.6), and solvent molecules can coordinate to the aliphatic hydrogens of the fluorene molecule in at least some cluster configurations, no direct evidence is found for the occurrence of proton transfer in S_1 in these systems.

Vibrational dynamics of aniline(Ar)₁ and aniline(CH₄)₁ clusters

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(Received 23 May 1989; accepted 18 July 1989)

The first excited electronic state (S_1) vibrational dynamics of aniline(Ar)₁ and aniline(CH₄)₁ van der Waals (vdW) clusters have been studied using molecular jet and time resolved emission spectroscopic techniques. The rates of intramolecular vibrational energy redistribution (IVR) and vibrational predissociation (VP) as functions of vibrational energy are reported for both clusters. For vibrational energy in excess of the cluster binding energy, both clusters are observed to dissociate. The dispersed emission spectra of these clusters demonstrate that aniline(Ar)₁ dissociates to all energetically accessible bare molecule states and that aniline(CH₄)₁ dissociates selectively to only the bare molecule vibrationless state. The emission kinetics show that in the aniline(Ar)₁ case, the initially excited states have nanosecond lifetimes, and intermediate cluster states have very short lifetimes. In contrast, the initially excited aniline(CH₄)₁ states and other intermediate vibrationally excited cluster states are very short lived (< 100 ps), and the intermediate cluster 0⁰ state is observed. These results can be understood semiquantitatively in terms of an overall serial IVR/VP mechanism which consists of the following: (1) the rates of chromophore to vdW mode IVR are given by Fermi's golden rule, and the density of vdW vibrational states is the most important factor in determining the relative [aniline(Ar)₁ vs aniline(CH₄)₁] rates of IVR; (2) IVR among the vdW modes is rapid; and (3) VP rates can be calculated by a restricted vdW mode phase space Rice-Ramsberger-Kassel-Marcus theory. Since the density of vdW states is three orders of magnitude greater for aniline(CH₄)₁ than aniline(Ar)₁ at 700 cm⁻¹, the model predicts that IVR is slow and rate limiting in aniline(Ar)₁, whereas VP is slow and rate limiting in aniline(CH₄)₁. The agreement of these predictions with the experimental results is very good and is discussed in detail.

7-Azaindole and Its Clusters with Ar, CH₄, H₂O, NH₃, and Alcohols: Molecular Geometry, Cluster Geometry, and Nature of the First Excited Singlet Electronic State

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(Received: September 11, 1989)

Mass-resolved excitation vibronic spectra of jet-cooled 7-azaindole and its clusters with Ar, CH₄, NH₃, H₂O, D₂O, CH₃OH, and C₂H₅OH are reported and analyzed with regard to molecular and cluster geometry and the nature of the first excited singlet state. Large changes in the various spectra are observed upon clustering and upon deuteration of 7-azaindole. The observed vibronic spectra of both 7-azaindole and its clusters can be rationalized with two general assumptions: (1) the hydrogen attached to the pyrrole nitrogen of 7-azaindole is out of the molecular plane in the first excited singlet state; and (2) the observed spectra are characterized by strong $n\pi^*-\pi\pi^*$ mixing not completely removed by the clustering. MOPAC calculations of molecular geometry suggest that the S_1 state is nonplanar. Additional cluster potential energy calculations suggest that the formation of cyclic hydrogen-bonded clusters is not likely for these gas-phase 1:1 or 1:2 7-azaindole/solvent clusters: the major gas-phase solvent clustering probably takes place at the π -system of the 7-azaindole molecule.

Observation and Geometry Assignment of the Conformation of Benzyl Alcohol in the Gas Phase

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Supersonic molecular jet laser spectroscopy is used to establish the perpendicular conformation of benzyl alcohol and a number of sterically unencumbered derivatives in the gas phase.

Observation and Geometry Assignment of Individual Conformations of Aryl Methyl Ethers in the Gas Phase

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^b Department of Chemistry, Condensed Matter Sciences Laboratory, Colorado State University, Fort Collins, Colorado 80523, U.S.A.

Supersonic molecular jet laser spectroscopy is used to observe the individual conformations of a number of aryl methyl ethers in the gas phase and to establish their planar conformations.

Spectroscopy and Structure of Jet-Cooled α -Methylstyrene

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In Final Form: February 14, 1990)

The ground (S_0) and excited (S_1) state geometries of α -methylstyrene (2-phenylpropene, 2) are investigated by mass-resolved excitation spectroscopy. In contrast to styrene, which has an intense spectral $S_1 \leftarrow S_0$ origin transition, α -methylstyrene exhibits a weak origin transition and a long progression in a low-frequency torsional mode, with an energy level spacing of $\sim 69 \text{ cm}^{-1}$. The intensity maximum of this progression occurs at the eighth peak position, indicating that the minimum-energy geometries of the ground and excited state are considerably displaced from one another. The torsional progression is assigned to the hindered rotation of the propenyl group with respect to the aromatic ring. Based on hot band transitions in the region of the origin, this torsional mode is assigned an energy level spacing of $\sim 32 \text{ cm}^{-1}$ in the ground state. Potential parameters derived from an analysis of the spectra are $V_2 \sim 0 \text{ cm}^{-1}$ and $V_4 \sim -150 \text{ cm}^{-1}$ for S_0 and $V_2 = 4867 \text{ cm}^{-1}$, $V_4 = -500 \text{ cm}^{-1}$, and $V_6 = -80 \text{ cm}^{-1}$ for S_1 . These two derived potential surfaces suggest that α -methylstyrene is nearly planar in its first excited singlet state and that the propene group is ca. 45° out of the aromatic plane in its ground state. An additional estimate of the S_0 geometry is made based on electronic transition energy for analogous systems, and this approach also yields a nonplanar ground-state geometry (ca. 30°) for α -methylstyrene. Analysis of the Franck-Condon intensity profile yields a displacement in the excited state for the angle between the aromatic and ethylenic groups of ca. 30° relative to the ground state. α -Methylstyrene is thereby suggested to be nearly planar in its first excited $\pi \rightarrow \pi^*$ state.

Supersonic Jet Studies of Benzyl Alcohols: Minimum Energy Conformations and Torsional Motion

Hoong-Sur Im,[†] E. R. Bernstein,^{a,†} Henry V. Secor,[‡] and Jeffrey I. Seeman^{a,‡}

Contribution from the Department of Chemistry, Condensed Matter Sciences Laboratory, Colorado State University, Fort Collins, Colorado 80523, and the Philip Morris Research Center, P.O. Box 26583, Richmond, Virginia 23261. Received March 21, 1990.
Revised Manuscript Received November 30, 1990

Abstract: Supersonic jet mass resolved excitation spectroscopy is employed to determine the minimum energy conformations of benzyl alcohol and a series of nine methyl-, ethyl-, fluoro-, and aminobenzyl alcohols. The interpretation of the mass resolved excitation spectra of these molecules leads to the assignment of specific molecular geometries for each system. The minimum energy conformation of the $-\text{CH}_2\text{O}$ moiety is determined to be perpendicular relative to the plane of the aromatic ring, i.e., $\tau(\text{C}_{\text{ortho}}-\text{C}_{\text{ipso}}-\text{C}_\alpha-\text{O}) = 90^\circ$. The hydroxy proton in the sterically unencumbered benzyl alcohol points toward the benzene ring. The potential energy barrier for the low-frequency torsional motion of the hydroxymethyl group arises mainly from an internal hydrogen-bonding interaction between the OH group and π -system of the ring. Using hindered rotor model calculations, the potential barrier to this torsional mode is determined to be $V_2 = -140 \text{ cm}^{-1}$ for S_0 and $V_2 = -330 \text{ cm}^{-1}$ and $V_4 = -3 \text{ cm}^{-1}$ for S_1 with a CH_2OH rotational constant of 0.52 cm^{-1} for both states. Similar potential barriers are observed for methyl-substituted benzyl alcohols. The potential energy barrier in S_1 changes significantly, however, for fluoro- and amino-substituted benzyl alcohols, as these substituents interact strongly with the π -electron system of the aromatic ring. For 2-fluorobenzyl alcohol, the nature of the low-frequency torsional mode changes to a combination of ($\text{O}-\text{H}\cdots\text{F}$) hydrogen motion and $-\text{OH}$ motion. The spectrum of benzyl fluoride is very similar to that found for benzyl alcohol, suggesting that the conformations of the two compounds are similar, e.g., $\tau(\text{C}_{\text{ortho}}-\text{C}_{\text{ipso}}-\text{C}_\alpha-\text{F}) = 90^\circ$.

**Spectroscopic Observation of Individual sp^3 -Nitrogen
Stereoisomers. Supersonic Jet Studies of
2-Aminobenzyl Alcohol¹**

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Received April 6, 1990

Revised Manuscript Received June 19, 1990

Assessment of the stereodynamics at the template associated with a pyramidal trivalent nitrogen is complicated by the presence of two low-energy processes, nitrogen inversion and internal rotation about various single bonds.¹⁻⁶ Supersonic molecular jet

**Excited state intermolecular proton transfer in isolated clusters:
1-naphthol/ammonia and water**

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(Received 7 January 1991; accepted 23 May 1991)

The excited singlet state intermolecular proton transfer reaction in jet-cooled clusters of 1-naphthol/ammonia and water is investigated employing mass resolved excitation, threshold photoionization, and emission spectroscopy. The complete data set indicates that no proton transfer occurs for 1-naphthol(NH_3)_{1,2} and (H_2O)_n, $n = 1, \dots, 20$ clusters. Proton transfer occurs for (at least) one configuration of the 1-naphthol(NH_3)₃ cluster, as well as all 1-naphthol(NH_3)_n, $n \geq 4$, clusters. The (at least) two configurations of 1-naphthol(NH_3)₃ clusters are distinguished by threshold photoionization studies. The 1-naphthol(NH_3)₃ cluster for which proton transfer is indicated has a threshold photoionization energy $\sim 2000 \text{ cm}^{-1}$ below the other 1-naphthol(NH_3)₃ cluster configurations. These results are employed to explain the previous discrepancy between static spectroscopic experiments and picosecond time resolved dynamic experiments concerning proton transfer in the 1-naphthol(NH_3)₃ cluster. Calculations of cluster geometry in 1-naphthol/ammonia and water cluster systems suggest some qualitative explanations of these observations.

Normal mode analysis of van der Waals vibrations

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(Received 25 January 1991; accepted 23 April 1991)

Two algorithms are presented for calculation of the van der Waals modes of weakly bound clusters. Both methods rely on the harmonic normal mode approximation and a chosen intermolecular potential. These calculational techniques differ specifically in the form of the force field employed: one method uses the total (both intra- and intermolecular) force field for the cluster and the other uses only the intermolecular force field. Both methods require rather elaborate coordinate transformation and their first and second partial derivatives; these are provided in detail. The two calculations generate eigenvalues and eigenvectors that are in complete agreement with one another for a given potential. The methods insure that the van der Waals modes are calculated at the proper cluster equilibrium configuration for which all torques and forces on molecules and/or atoms are effectively zero. Examples are presented for $(\text{H}_2\text{O})_n$ ($n = 2, \dots, 7$), benzene clustered with water, methane, and ammonia, and a number of different intermolecular potentials. Some of the observed heterogeneous cluster van der Waals modes are reassigned in light of these new results.

Excited state proton transfer in the S_1 state of 2-allylphenol, 2-propenylphenol, and 2-propylphenol and their van der Waals clusters with water and ammonia

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Excited state intramolecular and intermolecular proton transfer reactions in cold, isolated 2-allylphenol, 2-propenylphenol and 2-propylphenol, and their clusters with water and ammonia are investigated employing a combination of spectroscopic techniques (mass resolved excitation, threshold photoionization, dispersed emission), a semiempirical calculation (MOPAC 5) and a potential energy calculation of cluster structure. Threshold photoionization spectroscopy proves to be useful for the identification of molecular conformers in these systems but has mixed results for the identification of proton transfer in their clusters. The total collection of generated data suggests the following conclusions: (1) isolated, cold 2-allylphenol displays only one conformation which appears to have a significant stabilizing intramolecular interaction between the allyl group double bond and the hydroxyl group hydrogen atom; (2) 2-propenylphenol displays only one conformer; (3) 2-propylphenol has many conformations—probably more than five under the experimental conditions; (4) no evidence of intramolecular proton transfer can be found for these three isolated cold molecules; (5) no evidence for intermolecular proton transfer in water clusters has been found by any of the above techniques; and (6) evidence is found for intermolecular proton transfer in 2-allyl- and 2-propenylphenol(NH_3)_n, $n \geq 3$, in dispersed emission spectra. Dispersed emission spectra of 2-propylphenol(NH_3)_n, $n \geq 3$ are too weak to yield conclusive evidence for intermolecular excited state proton transfer. Potential energy minimization calculations of cluster geometry suggest that the difference between water and ammonia cluster behavior with regard to proton transfer arises because water molecules hydrogen bond with the hydroxyl group (both $\text{OH} \cdots \text{OH}_2$ and $\text{HO} \cdots \text{HOH}$) and each other while ammonia molecules are more evenly distributed over the entire molecular structure of the phenol moiety. Apparently, for efficient proton transfer to occur in clusters, the proton affinity of the solvent must be large and both the anion and the proton must be well solvated (stabilized) by the solvent.

ABSTRACT

Two-color mass resolved excitation spectra are obtained for the benzyl and "phenylnitrene" radicals. The spectrum previously assigned to the benzyl radical is generated by a species with mass 91 amu. This finding is consistent with the proposed $\text{C}_6\text{H}_5\dot{\text{C}}\text{H}_2$ benzyl radical structure. The origin of this $1\ ^2\text{A}_2 \leftarrow 1\ ^2\text{A}_1$ transition lies at $21,997\text{ cm}^{-1}$. The ionization energy for the benzyl radical is ca. 7.236 eV. The "phenylnitrene" radical spectrum is associated with a species of 90 amu. The "phenylnitrene" designation is not appropriate for this mass number: the suggested cyanocyclopentadienyl radical species ($\text{C}_5\text{H}_4\text{CN}$) is consistent with this mass. This radical has an ionization threshold of ca. 9.05 eV. Lifetimes are reported for a number of the vibronic states of both radicals.

Abstract

Atom-atom L-J (6-12-1) potentials are employed to calculate the cluster configurations of all local energy minima of benzene(N_2) $_n$ and (N_2) $_n$ clusters for $n=1, 2, \dots, 10$ and some benzene(Ar) $_n$ and N_2 (Ar) $_n$ clusters. The number of configurations increases exponentially and the binding energy range increases linearly with the number of solvent molecules for these clusters. Monte Carlo simulations are performed on the temperature behavior of the cluster potential energy, intermolecular distance, and some angular variables for benzene(Ar) $_n$, and benzene(N_2) $_n$ clusters.

Molecules comprising the cluster can undergo tunneling between the different potential energy minima at particular transition temperatures. This tunneling process can be viewed as a solid-solid or solid-liquid phase transition for the cluster.

Cluster properties vary smoothly with temperature if the temperature remains below the transition temperature. If an interpotential well tunneling occurs for molecules in a given cluster, a thermodynamic property or a proper order parameter can always be found which detects the tunneling in the cluster. A rapid molecular tunneling between various potential energy minima is indicative of the liquid phase. As in the bulk, not all system variables evidence this phase transition behavior with equal clarity or even equal intensity. Knowledge of cluster structure is therefore directly related to the understanding of cluster phase transitions.

A SPECTROSCOPIC CONFORMATIONAL STUDY OF ETHOXYBENZENE

Mark A. Young, Jeffrey I. Seeman, and Elliot R. Bernstein

An investigation of jet cooled ethoxybenzene and various substituted ethoxybenzenes, utilizing the techniques of one color time-of-flight mass spectroscopy and dispersed emission spectroscopy, is presented. Analysis of the accumulated data indicate that, under the conditions of our supersonic expansion, only one molecular conformation is present. The observations are consistent with an orientation placing the entire ethoxy group in the plane of the aromatic ring. These results are similar to those found for methoxybenzene.

DETERMINATION OF THE MINIMUM ENERGY CONFORMATIONS OF BENZYL ALCOHOL AND 2-PHENETHYL ALCOHOL

H. S. Im, E. R. Bernstein, J. I. Seeman

Abstract

Supersonic jet mass resolved excitation spectroscopy is employed to determine the minimum energy conformation of the alcohol group with respect to the benzene ring for benzyl alcohol (BA) and 2-phenethyl alcohol (2-PEA). The mass resolved excitation spectra of these molecules are presented and assigned. The C-O bond orientation in BA is determined to be perpendicular to the benzene ring ($\tau(\text{Cortho-Cipso-C}\alpha\text{-O}) = 90^\circ$) and in 2-PEA it is determined to be gauche with respect to the Cipso-C α bond ($\tau(\text{Cipso-C}\alpha\text{-C}\beta\text{-O}) = \pm 60^\circ$). By considering the OH \cdots π -electron cloud internal hydrogen bonding and the repulsive interaction between the non-bonding electrons on the oxygen atom and π -electron cloud, the hydroxyl proton in both molecules is suggested to be pointing toward the benzene ring.

ABSTRACT

The geometry of ortho-xylene is studied through supersonic jet cooling and one color mass resolved excitation spectroscopy. By examining the $S_1 \leftarrow S_0$ transition origin region of various (d_0 through d_2) methyl deuterated o-xylene species, the orientation of the two methyl groups can be inferred in both states. A comparison between the predicted and experimentally observed number and intensity of origin features for the various partially deuterated o-xylenes shows that two highly symmetric methyl group structures are possible, each structure having C_{2v} point group symmetry: one plane contains the ring and one C-H bond of each methyl group, while the other plane passes between the two methyl groups, perpendicular to the ring plane; and the line of intersection of these two vertical planes generates the C_2 axis. To elucidate which of the two experimentally determined structures is of lower energy, ab initio and semi-empirical calculations are performed. The results of these calculations allow us to assign a specific conformer as the minimum energy structure. The conformer assignment is consistent with microwave studies. In addition, a (repulsive) steric intramolecular (non-bonded) interaction between the two methyl groups is identified through potential energy calculations to be the most important interaction defining the lowest energy structure. These spectroscopic data, in conjunction with ab initio calculations, can be employed to investigate the ground and excited state potential energy surfaces.

R. Disselkamp, H. S. Im, E. R. Bernstein
J. I. Seeman, H. Secor

ABSTRACT

Mass resolved excitation spectra (MRES) are presented for a series of substituted anilines including 2- and 3-methylaniline, 2- and 3-ethylaniline, 2-aminobenzylamine, and 2-aminobenzyl alcohol. The observed spectra show the following phenomena: 1. nearly free internal rotation for the methyl substituent in the S_1 state; 2. long progressions in the C-C, C-N, and C-O side chain torsional motion; 3. inequivalence of the two amino hydrogens for both ring and side chain amino groups; and 4. probably two conformers for 2-aminobenzyl alcohol. Semi-empirical and ab initio calculations are performed on these systems to aid in the analysis of the potential surfaces and to elucidate the experimental results.

M. F. Hineman, S. K. Kim, E. R. Bernstein, D. F. Kelley

ABSTRACT

The first excited singlet state (S₁) vibrational dynamics of aniline(N₂)₁ clusters are studied and compared to previous results on aniline(CH₄)₁ and aniline(Ar)₁. Intramolecular vibrational energy redistribution (IVR) and vibrational predissociation (VP) rates fall between the two extremes of the CH₄ (fast IVR, slow VP) and Ar (slow IVR, fast VP) cluster results as is predicted by a serial IVR/VP model using Fermi's golden rule to describe IVR processes and a restricted RRKM theory to describe unimolecular VP rates. The density of states is the most important factor determining the rates. Two product states, 0⁰ and 10b¹, of bare aniline and one intermediate state $\overline{0^0}$ in the overall IVR/VP process are observed and time resolved measurements are obtained for the 0₀⁰ and $\overline{0^0}$ transitions. The results are modeled with the serial mechanism described above.

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